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Interrelation of Magnetic and Spectroscopic Properties for d^0, d^2 and d^3 Electron Structure in the VIIth Transition Group of Elements

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The electron structures d^0, d^2 and d^3 in the 7-th subgroup of the periodic system are found be particularly stable. The stability of these electron configuration doubtlessly depends on the principal quantum number «n» of the d electrons. We expected to answer the question on what is the type of this relationship and does it have periodic properties, using the magnetic spectroscopic and theoretical studies. The results of these studies for the compounds of Re, Tc and Mn are given in the present paper. The theoretical considerations were simplified owing to the fact that in the case of the d^2 and d^3 electron structure the ground terms are defined by the same quantum number L ($L=3$, terms ^4F and ^3F).

Introduction

The d^3 electron compounds. The stable compounds of these metals of the d^3 electronic structure have octahedral symmetry. The splitting of the d orbitals into two levels t_{2g} and e_g in the field of O_h symmetry and placing of these three electrons on the t_{2g} level, i.e. half-filling of this orbital (t_{2g}) is a doubtless reason of this structural stability.

In order to answer the question how this structural stability depends on the quantum number « n » of the d electrons, the absorption spectra of K_2ReCl_6, $(NH_4)_2TcCl_6$ and K_2MnCl_6 have been studies and their magnetic moments have been measured. The $ReCl_6^{2-}$ spectrum was studied and explained by Eisenstein[1] and Jørgensen[2] and we have confirmed their results. The three principal bands found in K_2ReCl_6 up to 20000 cm^{-1} are assigned to the following transitions:

$$a\Gamma_8 \rightarrow c\Gamma_8 \text{ and } \Gamma_6 \ (1100\ m\mu), \quad a\Gamma_8 \rightarrow \Gamma_7 \ (710\ m\mu),$$
$$a\Gamma_8 \rightarrow d\Gamma_8 \ (650\ m\mu).$$

The remaining bands in the ultra-violet region are the electron charge-transfer bands from the π orbital to the γ_5 one. We have determined experimentally the mean value of 7B (B - Racah parameter) from transitions

$$^4\Gamma_2 \rightarrow {}^2\Gamma_3,\ {}^2\Gamma_4 \quad \text{or} \quad a\Gamma_8 \rightarrow c\Gamma_8$$
$$\text{and} \quad {}^4\Gamma_2 \rightarrow {}^2\Gamma_5 \quad \text{or} \quad a\Gamma_8 \rightarrow \Gamma_7$$

This is equal to 3100 cm^{-1}, hence $B = 443\ cm^{-1}$. In the $TcCl_6^{2-}$ spectrum two groups of bands have been found which result from the transitions:[2]

$$^4\Gamma_2 \rightarrow {}^2\Gamma_4,\ {}^2\Gamma_3 \ (1050\ m\mu), \quad {}^4\Gamma_2 \rightarrow {}^2\Gamma_5 \ (720\ m\mu).$$

The mean value of 7B calculated for these transitions is equal to 3200 cm^{-1}, hence $B=456\ cm^{-1}$. The ultra-violet bands correspond to the electron charge-transfer bands. In $MnCl_6^{2-}$ three absorption bands are found at 560 mμ, 400 mμ and 230 mμ. On assuming that the band at 560 mμ corresponds to the $^4\Gamma_2 \rightarrow {}^4\Gamma_5$ transition we obtained: $\Delta = 17900\ cm^{-1}$. For the second maximum at 400 mμ which corresponds to the $^4\Gamma_2 \rightarrow {}^4\Gamma_4$ transition, the result is as follows: $\Delta + 12B = 25000\ cm^{-1}$. Hence $B = 591\ cm^{-1}$. The band at 230 mμ is the electron charge-transfer band.

The spectrum of K_2MnCl_6 has been also studied by Moews.[3] This author has found the following bands in the absorption spectrum: 15400 cm^{-1}, 27400 cm^{-1} and 33300 cm^{-1}. These bands were defined as very strong, strong and strong, respectively. He found one band at 16600 cm^{-1} in the reflectance spectrum of K_2MnCl_6 in the MgO diluent which was defined as very strong. Our studies on the absorption spectrum of K_2MnCl_6 (Fig. 1) did not confirm the intensities obtained by him. The reflectance spectrum of K_2MnCl_6 (Fig. 2) obtained by us does not also agree with that obtained by Moews.[3]

The author studied the reflectance spectrum of K_2MnCl_6 in MgO as a diluent which might effect partial reduction to MnO_2. The absorption measurements made by us on a K_2MnCl_6-MgO pellet have shown one very strong absorption band at 16600 cm^{-1}. In order to check the results, the reflectance of MnO_2+MgO has also been measured. In this case a very strong band

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(1) J. C. Eisenstein, *J. Chem. Phys.*, *34*, 1628 (1961).
(2) C. K. Jørgensen, K. Schwochau, *Z. für Naturforschung*, *20*, 65 (1965).
(3) P. C. Moews, *Inorg. Chem.*, *5*, 5 (1966).
(4) J. S. Griffith, The theory of transition-metal ions, Cambridge University Press, p. 810 (1961).

appears at about 16600 cm^{-1}, but it is broader and more diffuse.

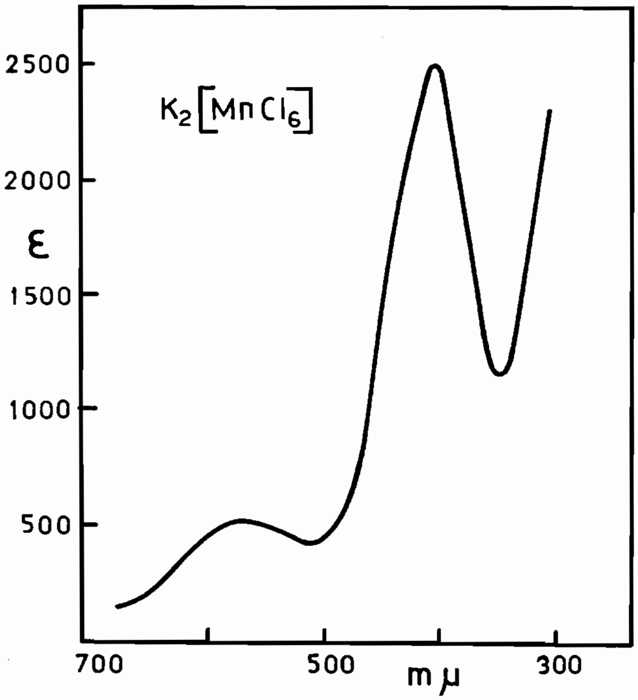

Figure 1. The absorption spectra of K_2MnCl_6 in 12 N HCl.

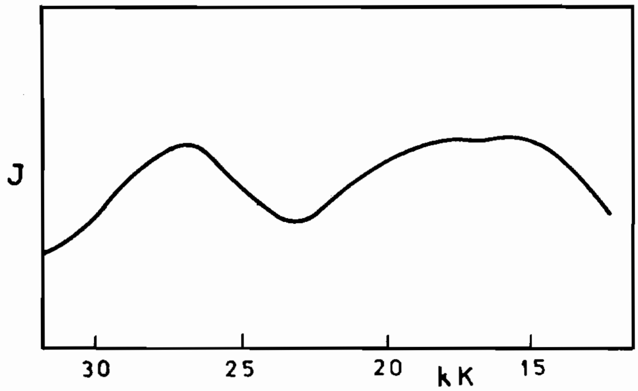

Figure 2. The reflection spectra of K_2MnCl_6.

Table I gives a comparison of particular parameters for these three complexes.

Table I.

Compound	Δ (cm^{-1})	B (of complex in cm^{-1})	B (of free ion in cm^{-1})
$MnCl_6^{2-}$	18000	591	1060^4
$TcCl_6^{2-}$	25000	456	700^4
$ReCl_6^{2-}$	29000*	443	640^4

* There is no agreement among various authors as to the magnitude of this value. The value given in Table 1 was taken from paper (2) whereas in paper (1) it is higher and amounts to 33500 cm^{-1}. We should take into account that in both these cases it is higher than that calculated for $TcCl_6^{2-}$.

The above values indicate that the weakest complex in $MnCl_6^{2-}$ and the strongest one $ReCl_6^{2-}$. A significant change of the Racah B parameter in the complex in comparison to B for a free ion in the case of $MnCl_6^{2-}$ shows that the electrons are diffused to ligands. This results in relatively ready oxidation to MnO_4^- or reduction to Mn^{2+} with formation of a very stable configuration with the d^5 electrons.

Since in the adjacent subgroup of the periodic system (particularly in Cr^{3+}) a stable d^3 electron configuration occurs, one may assume that the low stability of this structure in Mn^{4+} ion results probably from the increase of the charge.

The above compounds were subject to magnetic studies. The results are given in Table II.

Table II.

Compound	μ_{eff}	Weiss constant Θ
K_2MnCl_6	4.10	—22
$(NH_4)_2TcCl_6$	3.69	—39
K_2ReCl_6	3.55	—71

The negative values of the Weiss Θ constant indicate that antiferromagnetic interactions occur between the adjacent metal ions. This interaction is strongest in the case of $ReCl_6^{2-}$ and weakest in $MnCl_6^{2-}$. The magnetic studies made to 5°K by Busey and Sonder[5] have shown the occurrence of a characteristic maximum (for this type of interactions) on the magnetic susceptibility curve for K_2ReCl_6.

The change of Θ becomes comprehensible if the radial arrangement of 3d, 4d and 5d electrons is taken into account. The magnetic moments of all these complexes may be expressed by equation:

$$\mu = 3.87\,[1—(4\lambda/10\,Dq)] = 3.87\,[1—(4\,\xi_{nd}/30\,Dq]$$

where $$\lambda = \frac{\xi_{nd}}{2\,S},\ 10\,Dq = \Delta.$$

Taking into account both the relationship[5] $\xi_{5d} \cong 2\xi_{4d} \cong 5\,\xi_{3d}$ and the above equation it is made quite clear that the course of changes of the magnetic moments in the series Mn, Tc and Re is in agreement with former anticipations. This direction of changes has been predicted by Busey and Sender.[5]

The d^2 electron compounds. The compounds of the d^2 electron structure of metal ion are found in all the above elements. Manganese, unlike to technetium and rhenium, formes tetracoordinative compounds while the two latter ions form hexacoordinative compounds.

The magnetic studies made by us on the complexes shown in Table III have shown them to be weakly diamagnetic.

The magnetic studies made by Syrkin *et al.*[6] on the complexes $(ReO_2Py_4)Cl$ and $(ReO_2\,en_2)Cl$ have also

(5) R. H. Busey, E. Sander, *J. Chem. Phs.*, 36, 93 (1962).
(6) W. I. Belowa, J. K. Syrkin, E. G. Inolitow, A. S. Koletnikowa, G. K. Babieszkina, R. A. Dowlatszina, *Zh. Str. Khim.*, 5, 281 (1964).

Table III.

Compound	T	χ_M 10^{-6}
$(NH_4)_2TcOCl_5$	293	— 33
K_2ReOCl_5	293	—100
$K_3[ReO_2(CN)_4]$	293	—110
$(ChinH)_2ReOBr_5$	292	—288
$(ChinH)_2ReOJ_5$	293	—724
$[ReO(OH)en_2]Cl_2$	293	—135
$[Re(OH)_2en_2]Cl_3$	293	—165

shown a decrease of the magnetic moment. Other Re^V complexes containing the ReO_2^+ group have been also found to posses weak paramagnetic properties.[7] The magnetic properties of $[Re(en)_2O_2]Cl$, $[Re(en)_2O(OH)]Cl_2$, $[Re(en)_2(OH)_2]Cl$ have also been discussed by Murmann and Foerster.[8] On studying the magnetic properties of $ReOCl_5^{2-}$ Grove and Wilkinson[9] have found considerable paramagnetism. Our studies did not confirm their results.[10]

The absorption spectra were made for the obtained compounds of Re^V and Tc^V. The positions of the absorption bands for $TcOCl_5^{2-}$ and $ReOCl_5^{2-}$ are given in Fig. 3.

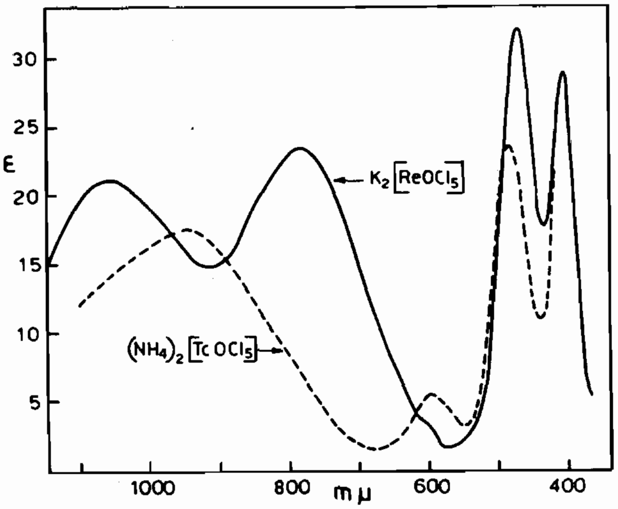

Figure 3. The absorption spectra of $TcOCl_5^{2-}$ and $ReOCl_5^{2-}$ in 12 N HCl.

Calculations made by us for these complexes (of C_{4v} symmetry) based on the crystal field theor have shown that these maxima ma be assigned to the transitions given in Table IV.

Table IV.

Transition	Position of absorption bands in cm^{-1}	
	$ReOCl_5^{2-}$	$TcOCl_5^{2-}$
$^1\Gamma_1(b_2^2) \longrightarrow {}^3\Gamma_3(b_2e)$	9091	
$\longrightarrow {}^1\Gamma_3(b_2e)$	12270	10526
$\longrightarrow {}^3\Gamma_2(b_1b_2)$	20534	16666
$\longrightarrow {}^1\Gamma_2(b_1b_2)$	23923	20619

The values of Δ and B for these complexes determined from the experimental data are equal to:

for $ReOCl_5^{2-}$ $\Delta = 25610\ cm^{-1}$ $B = 450\ cm^{-1}$

for $TcOCl_5^{2-}$ $\Delta = 22600\ cm^{-1}$ $B = 500\ cm^{-1}$

The values of $\Delta_1 = -3Ds + 5D\tau$ determined from the spectra of these complexes are equal to:

$ReOCl_5^{2-}$ $\Delta_1 = 15000\ cm^{-1}$

$TcOCl_5^{2-}$ $\Delta_1 = 14000\ cm^{-1}$

If $\Delta_1 > 9B + 3C$, then the ground term is the $^1\Gamma_1(b_2^2)$ term and the compounds is diamagnetic one. In the reverse case the $^3\Gamma_3(b_2e)$ term is the ground term and the compound is paramagnetic one.[11] The above tables indicate that the more stable compound is $ReOCl_5^{2-}$. Now, let us try to answer the question: why there is no compound of a formula $MnOCl_5^{2-}$?

The values of the crystal field parameters determined from the spectra indicate a very strong influence of the oxygen atom on the magnetic and spectroscopic properties of a given central ion. We have also calculated the scheme of molecular orbitals for the systems of this type. A considerable π-antibonding effect results in elevation of the e*(π) (dxz, dyz) orbital by about 15000 cm^{-1} with respect to a much less antibonding $b_2^*(\pi)$ orbital. The next orbital, $b_1^*(\sigma)$ is on the average about 25000 cm^{-1} higher than $b_2^*(\pi)$. At last $a_1^*(\sigma)$, in which the oxygen orbitals take part, is situated several thousand cm^{-1} higher than $b_1^*(\sigma)$.

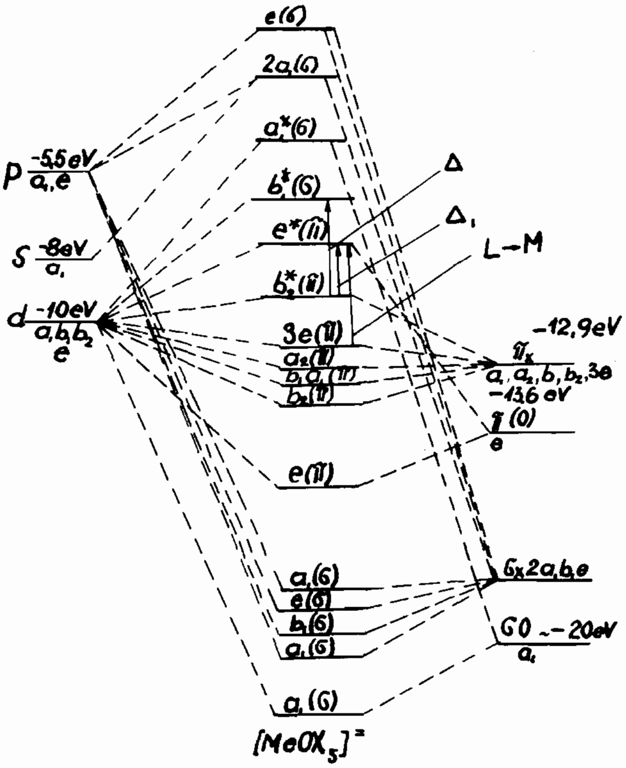

Figure 4. The scheme of molecular orbitals for the $MeOCl_5^{2-}$.

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(7) J. H. Beard, J. Casey, R. K. Murmann, *Inorg. Chem.*, *4*, 797 (1965).
(8) R. K. Murmann, D. R. Foerster, *J. Phys. Chem.*, 67, 1383 (1963).
(9) D. E. Grove, G. Wilkinson, *J. Chem. Soc.*, *A*, 1224 (1966).
(10) B. Jeżowska-Trzebiatowska, M. Bałuka, W. Wojciechowski, unpublished results.

(11) B. Jeżowska-Trzebiatowska, L. Natkaniec, *Zh. Str. Khim.* (in press).

Hence, a strong destabilizing effect of the oxygen on the central ion orbitals. If the compounds of such type are to be stable, the central ion could not have more than two electrons which will be placed on a weakly antibonding $b_2^*(\pi)$ orbital. In this situation all the complexes examined must be diamagnetic. This, in turn, requires high values of the Δ parameter, since in the other case, the paramagnetic complex with a T_d symmetry will be more stable. It is thus possible to substantiate the occurrence of such complexes (hexacoordinated) only for metals of the second and third transition periods. The same problem may be more quantitatively discussed as follows. From comparison of the B values determined for the above Re^{IV}, Tc^{IV}, Mn^{IV} complexes and these of Re^{V} and Tc^{V}, one may assume that the Racah B parameter for a hexacoordinative Mn^{V} compound will be equal to about 600 cm^{-1}. By using the relationship $C \approx 4B$ and the above condition for the occurrence of diamagnetism, we obtain

$$\bar{\Delta}_1 \approx 12600 \text{ cm}^{-1}.$$

From a comparison of changes of the Δ values in the series Re, Tc, Mn for both types of compounds and from the changes of Δ_1 for $ReOCl_5^{2-}$ and $TcOCl_5^{2-}$, one may assume that a hypothetical compound $MnOCl_5^{2-}$ would be paramagnetic with $\Delta_1 \approx 10000\text{-}11000$ cm^{-1} and 16000 cm^{-1}.

The decrease of the energy of the system in the octahedral Mn^{V} complex would be then equal to

$$2 \times 2/5\Delta \approx 4/5 \times 16000 = 12800 \text{ cm}^{-1}.$$

Now, let us consider a lowering of the energy in a tetrahedral complex. A well known ion is MnO_4^{3-}. Viste and Gray[11] have defined the value of Δ for this ion, on the basis of the molecular orbital theory and absorption spectra as equal to 11000 cm^{-1}. The energy decrease in this tetrahedral ion is following:

$$2 \times 3/5\Delta = 6/5 \times 11000 = 13200 \text{ cm}^{-1}.$$

It is apparent from a comparison of this value with the value obtained for a hypothetical Mn^{V} complex of O_h symmetry that the tetrahedral structure is more favorable.

The impossibility of the occurrence of $MnOCl_5^{2-}$ depends, of course, on many other factors which have not been taken into account in our considerations.

The d° electron compounds. The compounds of tetrahedral structure occur in all metals mentioned above on the 7th oxidation number i.e. for the d^0 electronic structure. For the compounds MnO_4^-, TcO_4^- and ReO_4^- the absorption spectra and magnetic susceptibility measurements have been made.

The positions of individual absorption bands in the spectra of these ions are given in Table V.

Viste and Gray[11] attribute these maxima to the transitions given in Table VI. The electron transitions corresponding to the absorption maxima were given by Viste[11] and Gray and are shown in Table VI.

The magnetic susceptibility measurements have been also made for these compounds. The results are given in Table VII.

Table V.

Compound	Position of absorption bands in cm^{-1}	
MnO_4^-	19000	32400
TcO_4^-	35000	41000
ReO_4^-	44000	49000

Table VI.

Compound	Transition Symbol and Position of Band in cm^{-1} $^1\Gamma_1$—$^1\Gamma_5$ $(t_1$—$2e)$;	$^1\Gamma_1$—$^1\Gamma_5$ $(3t_2$—$2e)$
MnO_4^-	19000	32400
TcO_4^-	35000	41000
ReO_4^-	44000	49000

Table VII.

Compound	Magnetic susceptibility in 298° K
MnO_4^-	$+0{,}20\ 10^{-6}$
TcO_4^-	$+0{,}10\ 10^{-6}$
ReO_4^-	$+0{,}16\ 10^{-6}$

It is apparent from the above table that MnO_4^- possesses the highest paramagnetism which is independent of temperature.

If we assume that the magnetic properties of these ions are described by equation

$$\chi_M = -\frac{N e^2}{6m c^2} \Sigma \bar{r}^2 + 2 N \sum_n \frac{|(n|\mu_z|O)|^2}{E_n - E_o}$$

then they depend on the magnitude of each particular component of this equation. The first component relates to diamagnetism, the second one-to Van Vleck's paramagnetism. $(n|\mu_z|O)$ is a matrix of the zeta component of the magnetic orbital moment which relates the ground stats to the excited on n, E_n-E_o is the energy interval for both these states. This equation indicates that Van Vleck's paramagnetism is inversely proportional to E_n-E_o. The experimental data: absorption spectra and magnetic measurements show that E_n-E_o is rising up in the order $Mn < Tc < Re$.

Hence the stability of these anions increases in the same order.

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(12) A. Viste, H. Gray, *Inorg. Chem.*, 3, 1113 (1964).